Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 75 (2015) 2068 – 2073
Energy Procedia

The 7th International Conference on Applied Energy – ICAE2015

Metallic nanoparticles for enhanced heavy oil recovery: promises and challenges

Kun Guo[1], Hailong Li[2], Zhixin Yu[1]*

1Department of Petroleum Engineering, University of Stavanger, 4036 Stavanger, Norway
2Department of Energy, Building and Environment, Mälardalen University, 72123 Västerås, Sweden

Abstract

With the increasing global energy demand, great attention has been focused on utilizing heavy oil and bitumen, which are potentially located ultra-deep underground and cannot be easily recovered. Numerous recovery approaches have been proposed for successful extraction of heavy hydrocarbons from ultra-deep reservoirs. However, these approached are often accompanied by high energy consumption, large amounts of wastewater generation, and undesirable environmental damage.
Nanotechnology has appeared as one of the promising technologies for in-situ heavy oil recovery, e.g., employing metal-based nanoparticles. In this article, we provide a brief overview of metallic nanoparticles for in-situ enhanced recovery of heavy oil. It gives a general introduction of the potential advantages of nanoparticle catalysts for heavy oil recovery and illustrates the improved recovery mechanism. Some technology challenges related to this promising technology will also be pinpointed. These technology challenges need to be solved through further research and development before field applications.

Peer-review under responsibility of Applied Energy Innovation Institute

Keywords: metal; nanoparticles; heavy oil; enhanced recovery; upgrading

1. Introduction

Challenges in meeting increasingly global energy demands have made it imperative to look for alternative energy sources to complement the conventional fossil fuel resources. Although eco-friendly renewable energy and biomass resources, including biodiesel and vegetable oils, have been produced in relatively large scale, however, these fuels are not likely to stand along as the solution for future energy demand, without the exploration and production of unconventional fossil fuels [1-3].

* Corresponding author. Tel.: +47-5183-2238; fax: +47-5183-2050.
E-mail address: zhixin.yu@uis.no.

Peer-review under responsibility of Applied Energy Innovation Institute
doi:10.1016/j.egypro.2015.07.294

Heavy oil as one unconventional crude with high abundance and wide distribution, is recognized as an important alternative of conventional fossil fuels. Nevertheless, due to the high viscosity, low hydrogen to carbon (H/C) atomic ratio and high content of sulfur and nitrogen [2], current technologies for heavy oil recovery still face numerous challenges, which necessitate further technology development in this field.

For the in-situ upgrading and recovery process, it is important to reduce the oil viscosity and improve the product quality that meets industrial specifications [2, 4]. Current enhanced recovery technologies can be divided into cold (or non-thermal) processes and thermal processes, among which the steam-assisted gravity drainage (SAGD) method has progressed and turned into the prevailing technique for heavy oil recovery [3]. In a typical SAGD process, steam is employed as the heat carrier and injected to reduce the viscosity of heavy oil as well as to enable the flow of oil fluid through porous sandrocks. Furthermore, when hydrogen is integrated with this thermal recovery method, the in-situ upgrading of heavy oil is realized with a series of chemical hydrogenation and cracking. However, this process is experienced with costly generation of steam and hydrogen, substantial carbon dioxide (CO_2) emissions, low displacement efficiency and insufficient degree of upgrading.

Nanotechnology has undergone continuous rapid development over the past decades and has found applications in electronics, materials, and pharmaceutical industry. Due to the unique properties of nanoscale materials, nanocatalysts have long been employed to catalyze the hydrocracking of heavy oil to transportable oils that meet pipeline and refinery requirements. The application of nanomaterials have also appeared as one of the promising technologies in exploration and production for the oil and gas industry.

Recently, metallic nanoparticles (NPs) assisted heavy oil recovery approach has been reported with desirable recovery efficiency at relatively low economic and environmental costs [5, 6]. Basically, a novel and stable aqueous suspension containing metallic NPs is injected along with heat and hydrogen reactant into the deep reservoir. These nanometer sized particles enable the sufficient contact between metallic catalysts and oil molecules and, consequently, effectively accelerate the cracking and hydrogenation of hydrocarbons. Noteworthily, these reactions are exothermic [7], thus generating more heat and gaseous products that further improve the oil detachment from rock surface. Benefiting from the advantages of nanomaterials, such as high inherent catalytic activity, high surface area to volume ratio, facile transport inside porous rocks and controllable synthesis for specific functions, this innovative approach for heavy oil production leads to significant enhancement of heavy oil upgrading and recovery.

Considerable efforts have been devoted to investigate various aspects of the technology ranging from controllable synthesis of NP catalysts to field application for upgrading and recovery processes [2]. Nonetheless, there are still technology issues remain unclear and need further exploration. This review briefly summarizes the recent advances in the synthesis, injection, and transport behavior of NPs for in-situ recovery. The possible enhancement mechanism and subsequent characterization of the upgraded oil products and quality have been summarized. Potential challenges and limitations for industrial implementation of this promising technology are also discussed.

2. Metallic NPs

2.1. Preparation of NPs

Synthesis methodology of metallic nanomaterials is enriched along with the fast advancement of nanotechnology in multidisciplinary applications. Precise manipulation of the size, shape, composition, type, and function has to some extent all been fulfilled according to the reasonable control of synthetic parameters. Generally, synthetic approaches can be categorized into top-down and bottom-up methods [1]. Top-down methods are normally associated with physical decomposition of bulk materials into nanoscale materials, such as milling and grinding. On the contrary, bottom-up methods involve the initial chemical reactions of molecular or atomic precursors and subsequent nucleation and growth to the formation of nanomaterials. It is worth mentioning that the chemical approaches are instrumental for the controllable synthesis of multifunctional nanomaterials.

Among different chemical approaches, the microemulsion method is widely used for the preparation of metallic NPs in heavy oil phase [2]. Typically, a water-in-oil (w/o) microemulsion is prepared by mixing water, oil and emulsifying agent, e.g., surfactants. A solution containing corresponding salt precursors is then added and blended uniformly with the w/o emulsion. Subsequently, another solution is added to activate the nucleation and growth of NPs, which exist inside individual water droplets covered by emulsifier and suspended steadily in the oil phase. Dispersed Fe, Ni, Cu, Cd, Pt and Pd NPs in w/o microemulsion have been prepared and applied to enhance in-situ upgrading and recovery of heavy oil and bitumen with interesting results [8]. However, once the NPs are applied to existing SAGD process with high temperature and heat, the enhanced heavy oil recovery is difficult to achieve due to particle agglomeration. Furthermore, the stability and mobility inside the porous rock grains as well as catalyst reclamation and recycle need further verifications. In addition, effect of NP size, concentration, exposed crystal facet, metal type, hydrophilic−lipophilic balance, and properties of injected hot fluids (interfacial tension, rheology, wettability etc.) on the catalytic activity and durability should be systematically investigated to optimize the upgrading and recovery processes.

2.2. Transport of NPs

Figure 1 shows the schematic diagram of NP assisted in-situ heavy oil recovery. The heavy oil are trapped at the pores between sandrock grains. Therefore, deployment of NPs inside viscous fluid is an important issue for NP assisted heavy oil recovery. Successful application of nanocatalysts in upgrading and recovery processes would depend largely on the availability of NPs to get contact with heavy hydrocarbon molecules both effectively and durably. Nanosized catalysts should theoretically be able to flow through the submicron and micron-sized channels that are filled with heavy oil. However, the high surface energy of NPs impels the spontaneous agglomeration and adsorption, causing the undesired deactivation of certain active sites. Possible coke deposition could also lead to catalyst poisoning and deactivation. Therefore, the motion behavior of NPs should be rationally designed and controlled to maximize the catalytic function. The NP catalysts need to be in appropriate regions as a kind of motion control to achieve the optimal catalytic performance.

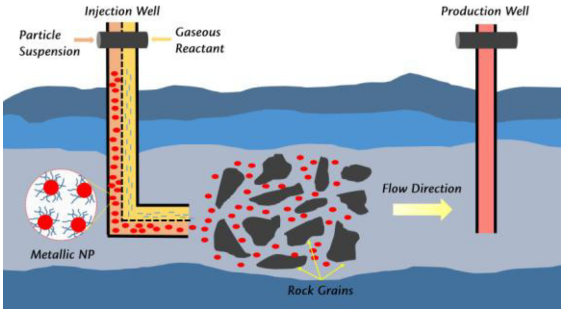


Fig.1 Schematic diagram of metallic NP assisted in-situ heavy oil recovery.

Recently, Nassar et al. [9] demonstrated the viable flow behavior of NPs in oil sands at temperature and pressure of typical SAGD process. Zamani et al. [10] reported that NPs could propagate through oil sands, even though part of injected NPs were retained inside the porous media, especially at the bed entrance. This retention was mainly attributed to agglomeration and irreversible adsorption. Also, effect of sand permeability, metal type and temperature on the transport behavior of NPs was explored experimentally by Hashemi et al [11]. Although the transport of NPs in reservoir is feasible, it should be noted that there is a lack of basic understanding of NPs behavior in reservoir rocks. Additionally, modelling of NPs behavior in porous media is too complex to be established convincingly.

3. Upgrading and recovery enhancement

3.1. Enhanced heavy oil recovery mechanism

In order to maximize recovery efficiency, the understanding of underlying mechanism is crucial in designing preferable catalysts. Conventionally, steam and hydrogen source play critical roles in heavy oil recovery, despite the high cost and massive CO_2 emission in the thermal processes. It is demonstrated that hydrogenation and hydrocracking reactions of heavy hydrocarbons are thermodynamically spontaneous when proceeding at favorable temperatures, while the reaction rates cannot be determined by this spontaneity. Therefore, the introduction of NPs is supposed to catalyze these chemical reactions with minimal heat consumption.

Catalytic hydrocracking of heavy hydrocarbons and the resulting viscosity reduction improve the fluidity of immobile heavy oil, which underlies the recovery enhancement. It should be noted that the major challenges come from the incorporation of NPs for hydrocracking processes. Furthermore, possible cleavage of C−C and C−S bonds resulted from the catalytic effect of NPs might also generate lightweight oil distillates, contributing to enhanced heavy oil upgrading and recovery [2].

Apart from this, wettability alteration is another plausible enhancement mechanism due to the surface modification of porous media by NPs adsorption. Owing to the nanometre size and large surface area of NPs, they would have a tendency to adhere to the rock surface, resulting in an important recovery mechanism, wettability alteration [2]. Once the rock wettability is tuned from oil wet to water wet, the oil droplets of the heavy hydrocarbons might be released, enabling the recovery enhancement. Besides, the incorporation of NPs would reduce the water-oil interfacial tension and improve the accessibility between active species and hydrocarbons molecules. This concept is extended by utilizing some metal oxide NPs (e.g., silica, titania, alumina) instead of commonly-used surfactant to stabilize the aforementioned emulsion and to support metallic NPs on the oxide surface, which is also the w/o interface. Accordingly, the resulting amphiphilic hybrid nanocatalysts can continuously catalyze the in-situ upgrading reactions [12]. Such catalyst and emulsion models highlight the significance of placing NP catalyst in appropriate regions as a kind of motion control to achieve the optimal catalytic performance.

3.2. Product characterization

Heavy hydrocarbons are composed of saturates, aromatics, resins and asphaltenes, which are featured by high viscosity, low API gravity (high density), low H/C ratio, and high sulfur, nitrogen and hetero-metals contents [2]. Hence, these properties should be characterized to evaluate the recovered product quality after the implementation of NPs.

Viscosity is regarded as one of the major factors for heavy oil to meet strict refinery plant and pipeline specifications [4]. Previous research has demonstrated viscosity reduction of Athabasca bitumen after NPs incorporation [13]. Also, API gravity was compared in absence and presence of NPs and remarkable API increment was observed for experiments with NPs, which demonstrated the feasibility of NPs for enhanced upgrading.

Similarly, the change of H/C ratio can also be measured as an indication of upgrading. Lighter products produced from the hydrogenation and cracking of heavy molecules will have higher H/C ratios.

Experimental results already demonstrated a significant improvement of H/C ratio by injecting NPs suspension into a batch reactor with hydrogen and sand for bitumen upgrading [14].

In a thermal cracking process without external hydrogen sources, the original hydrogen will be redistributed in the feedstock, which means the generation of light components with increased H/C ratio as well as even heavier coke. According to this theory, carbon residue could be measured as another indicator for the extent of heavy oil upgrading, i.e., products with improved quality will possess a lower content of carbon residue.

Furthermore, it is suggested that inhibition of coke formation is closely associated with quality enhancement. Because of the improved transfer of hydrogen atom to free radicals by injected NPs, the coke formation is largely depressed. Researchers also proposed that the presence of NPs could bring more reaction paths for free radicals [13].

Sulfur removal is necessary in any oil refining processes due to the strict environmental regulations on transportation fuels. Fortunately, due to the nanosize and high surface area, the interaction between NPs and C−S bonds is enhanced, which improves the hydrodesulphurization reaction that involves the production of hydrogen sulfide and desulfurized compounds. An early study has demonstrated marked sulfur removal effect with the addition of NPs [15], which again confirms the effectiveness of NPs application for enhanced upgrading and better product quality.

4. Technology challenges

Although the successful upgrading and recovery enhancement with the incorporation of metallic NPs has been demonstrated in previous studies, it should be noted that many experiments are conducted in the absence of porous media [13]. In addition, for the current prevailing in-situ heavy oil upgrading and recovery processes, many unknown factors still remain to be elucidated. Further addition of the catalytic NPs will improve the complexity of the existing methods [2]. Therefore, with the ultimate goal of industrial application, there are still numerous challenges to be addressed regarding this promising technology.

Chemical and engineering challenges associated with metallic NPs should be treated as high priority issues. For large scale industrial application, chemical approaches for stable and reliable preparation of metallic NPs with an economically acceptable cost need to be established [13]. Also, effective separation, recycling and post-treatment of the NPs from underground reservoirs are necessary for an economical and sustainable operation [1]. Particle agglomeration and adsorption at high reaction temperatures should be controlled to ensure the transportation of metallic nanoparticles in the porous sandrocks.

As a requisite co-reactant in the upgrading processes, the consumption of a large amount of hydrogen is also an important issue [2]. Inevitably, the production and delivery of hydrogen will involve large investment. Furthermore, the thermal reactions in presence of hydrogen at high pressure and temperature should proceed steadily and safely.

Environmental footprint is another challenge to be minimized. During in-situ upgrading and recovery processes, emission of pollutants, such as CO_2 and sulfur and nitrogen-containing gases, should be reduced to reasonable levels. Last but not the least, formation damage is also a problem that demands special attention.

5. Conclusions

Stable suspension containing uniformly dispersed metallic NPs can be tailor synthesized and injected in heavy oil reservoirs for in-situ upgrading and improved recovery. Viability of NP transport through the porous media have been testified experimentally. Benefiting from the nanoscale size, multiple reactive sites and superior catalytic activities, the hydrogenation and hydrocracking reactions are accelerated. The inhibition of coke formation is attributed to the improved hydrogen transfer to free radicals by NPs. Furthermore, wettability alteration resulted from the surface adsorption of NPs facilitates oil droplet release from the porous media. These mechanisms could be partly responsible for the heavy oil recovery enhancement, which is characterized with reduced viscosity, increased API gravity and H/C ratios, decreased content of sulfur and nitrogen, and inhibited coke formation.

Although the metallic NPs have been demonstrated as a promising eco-friendly technology, the metal nanoparticles assisted recovery process still faces a few challenges, which need to be researched for its successful implementation in the fields.

Acknowledgements

The authors would like to thank National IOR Centre at UiS who financially supported this project.

References

[1] Almao PP. In situ upgrading of bitumen and heavy oils via nanocatalysis. Can. J. Chem. Eng. 2012; 90: 320-9.

[2] Hashemi R, Nassar NN, Pereira Almao P. Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges. Appl. Energy 2014; 133: 374-87.

[3] Rana MS, Sámano V, Ancheyta J, Diaz JAI. A review of recent advances on process technologies for upgrading of heavy oils and residua. Fuel 2007; 86: 1216-31.

[4] Martínez-Palou R, Mosqueira MdL, Zapata-Rendón B, Mar-Juárez E, Bernal-Huicochea C, de la Cruz Clavel-López J, Aburto J. Transportation of heavy and extra-heavy crude oil by pipeline: A review. J. Pet. Sci. Eng. 2011; 75: 274-82.

[5] Li L, Yuan X, Sun J, Xu X, Li S, Wang L. Vital role of nanotechnology and nanomaterials in the field of oilfield chemistry. International Petroleum Technology Conference. 2013, Beijing.

[6] Loria H, Trujillo-Ferrer G, Sosa-Stull C, Pereira-Almao P. Kinetic modeling of bitumen hydroprocessing at in-reservoir conditions employing ultradispersed catalysts. Energy Fuels 2011; 25: 1364-72.

[7] Ancheyta J, Sánchez S, Rodríguez MA. Kinetic modeling of hydrocracking of heavy oil fractions: A review. Catal. Today 2005; 109: 76-92.

[8] Capek I. Preparation of metal nanoparticles in water-in-oil (w/o) microemulsions. Adv. Colloid Interface Sci. 2004; 110: 49-74.

[9] Zamani A, Maini B. Flow of dispersed particles through porous media — deep bed filtration. J. Pet. Sci. Eng. 2009; 69: 71-88.

[10] Hashemi R, Nassar NN, Pereira-Almao P. Transport behavior of multimetallic ultradispersed nanoparticles in an oil-sands-packed bed column at a high temperature and pressure. Energy Fuels 2012; 26: 1645-55.

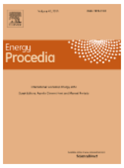
[11] Zamani A, Maini B, Pereira-Almao P. Experimental study on transport of ultra-dispersed catalyst particles in porous media. Energy Fuels 2010; 24: 4980-8.

[12] Crossley S, Faria J, Shen M, Resasco DE. Solid nanoparticles that catalyze biofuel upgrade reactions at the water/oil interface. Science 2010; 327: 68-72.

[13] Hashemi R, Nassar NN, Pereira Almao P. Enhanced heavy oil recovery by in situ prepared ultradispersed multimetallic nanoparticles: A study of hot fluid flooding for athabasca bitumen recovery. Energy Fuels 2013; 27: 2194-201.

[14] Galarraga CE, Pereira-Almao P. Hydrocracking of athabasca bitumen using submicronic multimetallic catalysts at near in-reservoir conditions. Energy Fuels 2010; 24: 2383-9.

[15] Hashemi R, Nassar NN, Pereira Almao P. In situ upgrading of Athabasca bitumen using multimetallic ultradispersed nanocatalysts in an oil sands packed-bed column: Part 1. Produced liquid quality enhancement. Energy Fuels 2013; 28: 1338-50.



Biography

Zhixin Yu is Professor at Department of Petroleum Engineering, University of Stavanger, Norway. He received his doctorate in Chemical Engineering from Norwegian University of Science and Technology (2005). He has then worked as research scientist at SINTEF, IRIS and Statoil. His main research interests are energy production by nanotechnology.